Spanish biofuels heating value estimation based on structural analysis

Ana Álvarez, Consuelo Pizarro*, Roberto García, Julio L. Bueno

Department of Chemical and Environmental Engineering, Faculty of Chemistry, University of Oviedo. Ave. Julián Clavería, 33006, Oviedo, Spain

*corresponding author

Telephone: +34 985 103438

Fax: +34 985 103434

e-mail: pizarroconsuelo@uniovi.es

Abstract

The importance of waste biomass as an energy source is likely to increase during the coming years as a result of European energy policy objectives, and because of the wide range of possibilities that it offers: it is a cheap fuel, widespread, and available in large quantities. In addition to crops and forestry operations, the Spanish fruit, olive and wine industries generate large amounts of currently undervalued solid wastes such as stones, branches, pulps or pomaces. The use of these by-products offers environmental benefits like removing waste and preventing fires at the same time as providing an energy yield. A proper energy valorization will require a complete physicochemical characterization. In this article, a structural and thermal characterization is developed from twenty samples from the olive and wine industries, as well as from forest and agro wastes. In addition, predictive equations are proposed to determine higher heating value (HHV) from chemical composition. For this

purpose, the chemical extraction method (also called the ‘classic’ method) was used, and results were obtained in accordance with the data shown in the bibliography. Two predictive equations were developed: one based on lignin and hemicellulose content, and the other based on lignin quantity. Both present an absolute average error (AAE) of 0.87% and 1.13%, respectively.

Keywords: Biomass**,** high heating value**,** structural analysis**,** chemical composition

1. Introduction

During recent years, waste biomass has gained in importance as an energy feedstock due to requirements for developing various renewable energy sources to reach European goals for the years 2020 (the “three 20s” target) and 2050.

Among complementary energy resources, biomass offers great possibilities, including those involving direct (combustion) procedures and indirect (extractive or transformative) procedures of reuse, recovery and revaluation (Barbanti et al., 2014). Since biomass as waste is cheap and available nearly everywhere (Masnadi et al., 2014), and is also responsible for lower emissions of environmentally detrimental gases like sulphur dioxide (SO_2) and nitrogen oxides (NO_x), the combustion of biomass also plays a positive role in reducing global acid rain formation (Zhang et al., 2010). In addition, biomass contributes approximately 14% of worldwide energy consumption (Demirbas and Demirbas, 2007), meaning 63% of all renewable energy sources (García-Maraver et al.,

2012). The work of (Krzyżaniak et al., 2014 and 2015 *in press*; Salaheldeen et al., 2014), are worthy of mention as recent contributions. Woody crops management, like orchards, olive groves or vineyards, generate huge amounts of waste (Godin et al., 2013).

To achieve an efficient reuse of residual vegetable biomass, the availability of the raw matter (quality, quantity, location of origin) must be reconciled with the characteristics of the chosen or available technical alternatives (fundamentals of procedures, optimal design capacity and location of the consumers of commercial energy). The technical and economic success of most of the options is thus strongly associated with geography, climate and customer requirements.

In Spain, the biggest potential biomass source belongs to Andalucía and Castilla-La Mancha, which together provide nearly 50% of all woody crop wastes (Rosúa and Pasadas, 2012). It should be noted that, due to high production, olive and wine industrial wastes are plentiful in Spain, but not sufficiently valued. These two industries produce a large quantity of several types of biomasses with different properties. Spain's Surfaces and Crop Yields Inquiry (ESYRCE) shows an overall vineyard-crop cultivation area of 963,644 hectares, while the olive growing area amounts to 2,593,523 hectares, meaning 5.7% and a 15.1%, respectively, of overall cultivated surface area in Spain.

The main organic wastes obtained from the olive industry are olive pomace, extracted olive pomace (coming from oil mills), olive vegetable water (also called "alpechín"), a mixture of olive vegetable water and pulp (known as

70 “alperujo”) and, in lower quantities, olive stones. Figures 1a and 1b show a
71 diagram of olive oil production using the three existing procedures and an
72 extractive plant flow chart.

73 The main organic wastes from the wine industry are pomace (pressed grape
74 waste), lees (fermentation and maturing precipitates), wine wash water
75 (vinasse), and the grape stalks that are separated in the destemmer. Figure 2
76 shows a white wine production chart, indicating wastes obtained in each phase
77 of production. Red wine production is slightly different, but the same types of
78 wastes are obtained.

79 Figures 1a, 1b and 2 illustrate olive and wine production wastes organized
80 according to colour. Thus, the green boxes are solid wastes, which are the
81 subject of interest in this work, while the liquids, which are not studied here,
82 appear in yellow. Finally, end or tail products for each process are marked in
83 blue, and sub-products and other wastes are marked in grey.

84 In addition to the woody crops, there are other biomass sources like the
85 harvesting of shrubland areas or of whole trees not necessarily coming from
86 agro-crops. The thinning out of wooded areas and the proper treatment of
87 shrubs is a useful tool for preventing disease while sustainably exploiting
88 Spain’s woody regions. Olive groves, vineyards and orchards require regular
89 pruning, which generates a huge amount of biomass available for energy use
90 (Spinelli and Picchi, 2010).

91 On the other hand, extensive neglected scrubland zones are an undesirable
92 fuel source and the main spreader of forest fires in Spain, and they represent a

significant environmental impact because of adding to the greenhouse effect. The valorization of these wastes could be an incentive for environmental clean-up, considering that forestry biomass reaches 18,715,359 tonnes per year, while the whole biomass potential in Spain alone reaches 88,677,193 tonnes per year, as shown in Table 1.

In fact, not all of these waste materials are usually properly managed. For example, prunings are commonly burned in the same place where they are gathered (Velázquez-Martí et al., 2011). The energy use of these wastes not only contributes to sustainable energy production, but also improves the management of waste materials *in situ*.

Taking into account the lack of accurate biomass standardization, particularly in terms of physicochemical, process and environmental indicators, the evaluation and selection of raw materials for obtaining better process efficiencies presents many difficulties. Therefore, a proper characterization is required for the adequate use the wastes previously described.

The properties of commercial fuel are usually well known. Nevertheless, some waste-biomasses, like the ones studied in this article, are not fully standardized and do not follow any specific, existing normative (that for pellets, for example), so it becomes necessary to study their characterization in depth. This research group has previously developed studies on the proximate and ultimate analysis of biomass fuels (García et al., 2014a, 2014b). A chemical composition study of those materials is thus required in order to fully complete this work.

The main structural components of biomass are cellulose, hemicellulose and lignin. Cellulose appears in the largest quantities in lignocellulosic biomass, which is a linear polymer formed by ß-glucose units joined together by ß-1,4-glucosidic bonds. In addition, as a whole, it possesses a fibrous structure in which hydrogen-bridge bonds between hydroxyl groups of alternate glucose chains are formed, making it tough and insoluble to water (Smook, 2002).

Hemicelluloses, as cellulose, are polymers made of pentoses, hexoses and uronic acid units. They are smaller than cellulose and, also being amorphous polysaccharides, each unit generally contains more than one kind of sugar (Carrier et al., 2011).

Lignin is a 3D polymer formed by three units of phenylpropane (conipheryl, sinapyl and coumaryl alcohols). Lignin possesses a huge variety of functional groups and 10 different bond types (Tejado et al., 2007).

Figure 3 shows the 3D order of the main biomass chemical components as well as the proportion in which they usually appear. The images were obtained using a Scanning Electron Microscope (SEM), at a magnification of 110x, 250x and 130x for lignin, cellulose and hemicellulose, respectively.

In Figure 3, depicts how cellulose appears as long fibres surrounded by a net of hemicellulose, joined by hydrogen-bridge bonds. Lignin is placed as a matrix between the strings formed by the merging of cellulose and hemicellulose. These fractions are joined by hydrogen-bridges and covalent bonds (benzyl esters, benzyl ethers and phenyl glycosides (Smook, 2002)).

Chemical composition is closely related to the potential applications of a material and therefore to its energy use because higher heating value (HHV) greatly depends on these compounds. This relationship can be observed by the existence of varying HHV-predictive equations based on chemical composition.

The common methods for determining Lower Heating Values (LHV, defined as excluding heating losses through sub-products of combustion) and Higher Heating Values (HHV), may be classified into three inter-connected basic groups: theory, direct experimentation and empirical correlations. In fact, thermodynamic models based on rigorous state theories have the drastic inconvenience of needing detailed and precise analysis of all of the thousands of molecules present in such a natural product in order to reliably integrate (if previously available) a significant number of reactive internal energies or enthalpies. Experimentation must be carried out using original and sophisticated laboratory techniques or by precise, consolidated and commercially well-developed ones, e.g., by calorimetric bomb. Empirical estimations attempt to shortcut time-consuming experimental calculations, thus reaching the typical engineering compromise between requirements and accuracy. This question has been thoroughly discussed in some of our previous contributions (García et al., 2014a, 2014b).

The purpose of these last methods, particularly useful in a practical context, is to avoid slow and cumbersome procedures correlating HHV and LHV with less onerous available data (i.e., structural analysis is preferable to elemental analysis) while maintaining reliability within acceptable limits.

160 This work proposes several equations, based on experimentally obtained data,
161 which enlarge the inventory of equations previously proposed by other authors,
162 and which is summarized in Table 2.

163 As can be seen in Table 2, equations obtained after bibliographical review can
164 be categorized for specific biomass groups (like TIL or WHI, exclusively for
165 woody fuels) or with broad, general applicability. They can also be defined from
166 just one biomass fraction (like ACA or DEM01, 03 and 04) or from more than
167 one, such as J&G, which uses all structural biomass components in their
168 proposed correlation. In addition, fractions used to calculate HHV values may
169 be expressed on a different basis by different authors.

170 The new equations proposed here for estimating HHV are based on the
171 chemical structural analysis of biomass samples.

172

173 **2. Samples and methods**

174 2.1. Samples

175 Chemical composition and HHV were determined for twenty biomass samples
176 belonging to agro-forestry wastes and industrial wastes. For the purpose of
177 illustration, Figure 4 shows some of the analyzed samples.

178 As a pre-treatment to sort and isolate the analyzed fractions, all studied
179 samples were grinded and milled until particle size was in the range of 250-
180 500 μm (TAPPI, 2007).

2.2. Experimental procedure

Biomass chemical composition can be obtained through a chemical extraction process that is summarized in Figure 5. Data for different fractions are expressed on the basis of free dry, ash and extractives. Every experimental run, except the singular extractive determinations, was performed three times to assure reproducibility according to a pre-established accuracy.

2.2.1. Sample preparation

Before quantifying different biomass fractions, it was necessary to homogenize sample size distribution. Once this was achieved, samples were subjected to a two-stage extraction process to eliminate a group of substances known as "extractives" that may interfere with a rigorous characterization. The first of these stages consisted of an acetone treatment in a Soxhlet extractor lasting 7-8 hours to get rid of resins, waxes, sterols, fats and fatty acids. The second phase was carried out with boiling water for 1 hour: tannins, gums, sugars and coloured matter were removed. Once both phases were completed, the refined biomass was air-dried to reduce its moisture content to below 15 %.

2.2.2. Holocellulose fraction determination

This quantity was obtained from an extractive-free biomass using an acetic acid and sodium chloride treatment, according to the ASTM D-1104 standard (Test for Holocellulose in Wood) (ASTM International, 1978).

2.2.3. Cellulose fraction determination

Cellulose quantity was determined from the holocellulose fraction obtained previously. This procedure consisted of a sodium hydroxide treatment according to the TAPPI T 212 standard (TAPPI, 2002). Hemicellulose content can be derived from the difference between holocellulose and cellulose quantities.

2.2.4. Lignin fraction determination

Lignin quantification was determined according to the NREL/TP-510-42618 standard (A. Sluiter et al., 2008), which consists of a two-stage acid hydrolysis, with the first step using concentrated sulphur acid and the second stage with the same diluted agent at high pressure.

2.2.5. Ash fraction determination

An ash quantification test, following the NREL/TP-510-42622 (A. Sluiter et al., 2005) standard, was carried out. This procedure consists of a thermal treatment of each fraction at 600º C for every previously calculated fraction.

2.2.6. HHV determination

The quantification of this energy content indicator was carried out using an IKA Werke C5000 calorimetric bomb, and following the ASTM E711 (ASTM International, 1987) standard. HHV data used in this article are shown in Table 3.

3. Results and discussion

3.1. Structural Analysis

Analysis data obtained by chemical extraction for each studied sample are shown in Table 4. Contents of structural components are normalised to 100%.

Analysed samples demonstrate a wide range of extractive matter ratios, from 0.35% for chestnut tree chips, to 67% for extracted olive pomace. The variability in structural component quantity is not as wide. As expected, values between 21% and 39% were found for lignin, but grape stalk was exceptional with a value of over 50%. The range for cellulose was 27% to 60%, while for hemicellulose the indices obtained were between 10.68% for olive stone and 42.79% for corncob. The exception, once again, was grape stalk, which exhibited just 2%. These results were been compared with others available in the literature such as those of (Vassilev et al., 2012; Mendes et al., 2013; Prozil et al., 2012; Matos et al., 2010), and there is a notably strong agreement among them.

3.2. HHV estimations

The first step consisted of determining which of the parameters is the most influential on an HHV estimate. Matlab's command *corrcoef* was used for this purpose. R and P matrixes were obtained, with R being a squared matrix of correlation coefficients, with as many rows and columns as compared variables. The P matrix contains the P-values, and is the result of checking the non-correlation hypothesis. The results for the tested variables are shown in Table 5.

According to the statistical protocol, the closer to 0 a P-value comes, the higher the probability of dependence there is between the correlated variables, so the corresponding R-values can be considered significant. An examination of Table 5 shows that correlations obtained for cellulose demonstrate P-values much higher than 0.05, so the relationship between HHV and this parameter is meaningless. Therefore, no cellulose-based correlations have been proposed. Nevertheless, the P-values obtained for lignin and hemicellulose were low, so these fractions should be considered as important in determining HHV.

After choosing the most important parameters, the Matlab command *regress* is used to obtain linear equations based on the selected parameters or linear combinations thereof. The correlations thus obtained were statistically checked using three criteria: *absolute average error* (AAE), *average bias error* (ABE), relative errors commonly used by several authors (Callejón-Ferre et al., 2014; Sheng and Azevedo, 2005) and *average absolute deviation* (AAD). They are defined as follows:

$$\mathrm{AAE}\ (\%) = \frac{1}{\mathrm{n}}\left[\sum 100\,\frac{|\mathrm{HHV_{calc}}\text{-}\mathrm{HHV_{exp}}|}{\mathrm{HHV_{exp}}}\right] \quad (1)$$

$$\mathrm{ABE}\ (\%) = \frac{1}{\mathrm{n}}\left[\sum 100\,\frac{(\mathrm{HHV_{calc}}\text{-}\mathrm{HHV_{exp}})}{\mathrm{HHV_{exp}}}\right] \quad (2)$$

$$\mathrm{AAD} = \frac{1}{\mathrm{n}}\left[\sum\left|\mathrm{HHV_{calc}}\text{-}\mathrm{HHV_{exp}}\right|\right] \quad (3)$$

Proposed equations and their error values are shown in Table 6. Based on structural analysis data, these equations show a lower value for AAE (1.13%)

compared to the AAE values of correlations based on proximate or elemental analysis data (5% to 7%) proposed by the authors (García et al., 2014a, 2014b).

In Figure 6, the relationship between the predicted values (X-axis) and those obtained experimentally (Y-axis) using data from the bibliography (Telmo and Lousada, 2011; Demirbaş, 2001) are shown in order to validate the equations proposed in this article.

As can be seen in Figure 6, all of the data are within a range of 13% of error with respect to the experimental values.

4. Conclusions

Chemical analysis confirmed that the main component of lignocellulosic biomass is cellulose (27% to 60%), followed by lignin (21% to 39%) and hemicellulose (10% to 43%).

Results obtained and shown in this article are in good agreement with those obtained by other authors.

Higher Heating Value is related to the content of biomass structural compounds, mainly lignin. Existing equations for predicting HHV are focused on specific biomass groups, while the ones proposed in this work have a general character.

The equations presented in this work depend on structural biomass components, predicting HHV values with an average absolute error (AAE) of less than 1.13%.

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Figure captions

Fig. 1a. Olive oil production flowchart: olive oil mill (hydromechanical method)

Fig. 1b. Olive oil production flowchart: olive pomace extractor (mass transfer method)

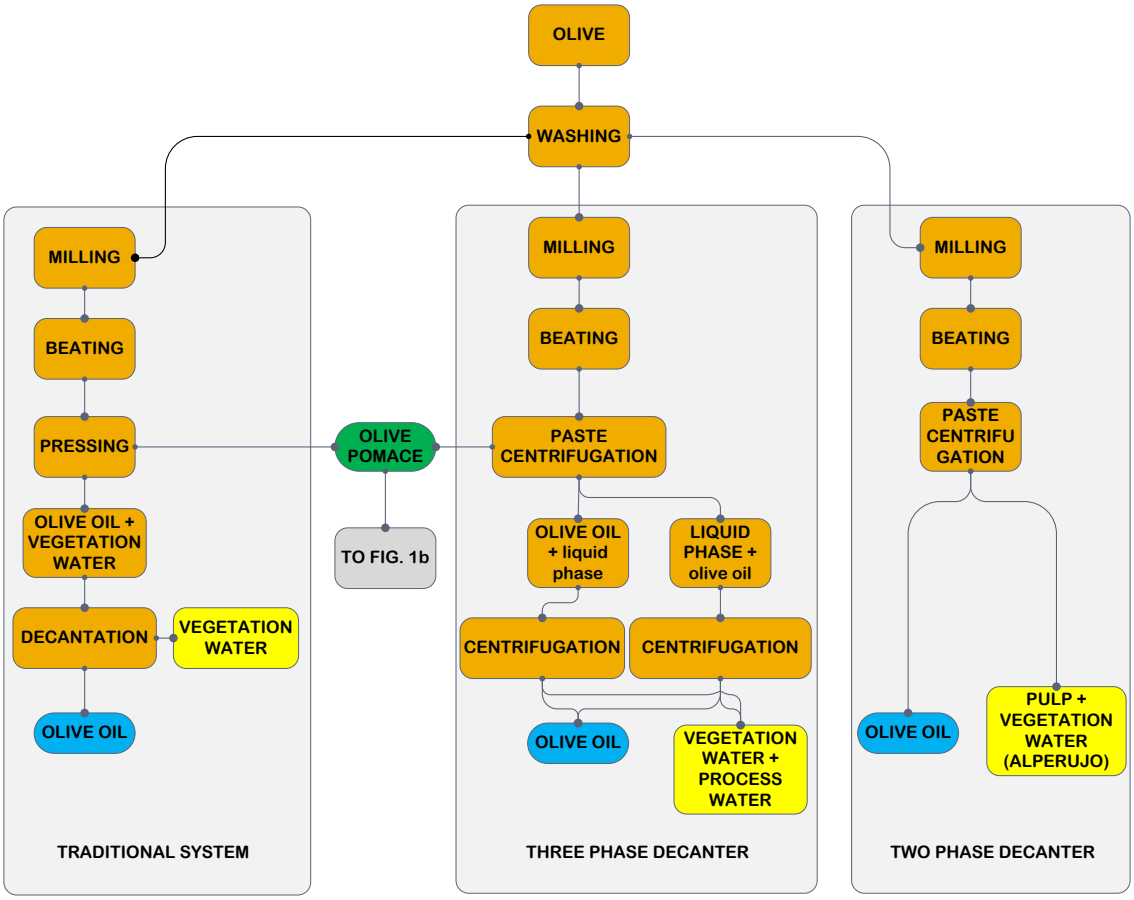
Fig. 2. White wine production flowchart

Fig. 3. 3D biomass structure

Fig. 4. Pictures of the samples analysed

Fig. 5. Experimental procedure chart

Fig. 6. Predicted vs. experimental HHV from data in the bibliography



441

442 **Fig. 1a.** Olive oil production flowchart: olive oil mill (hydromechanical method).

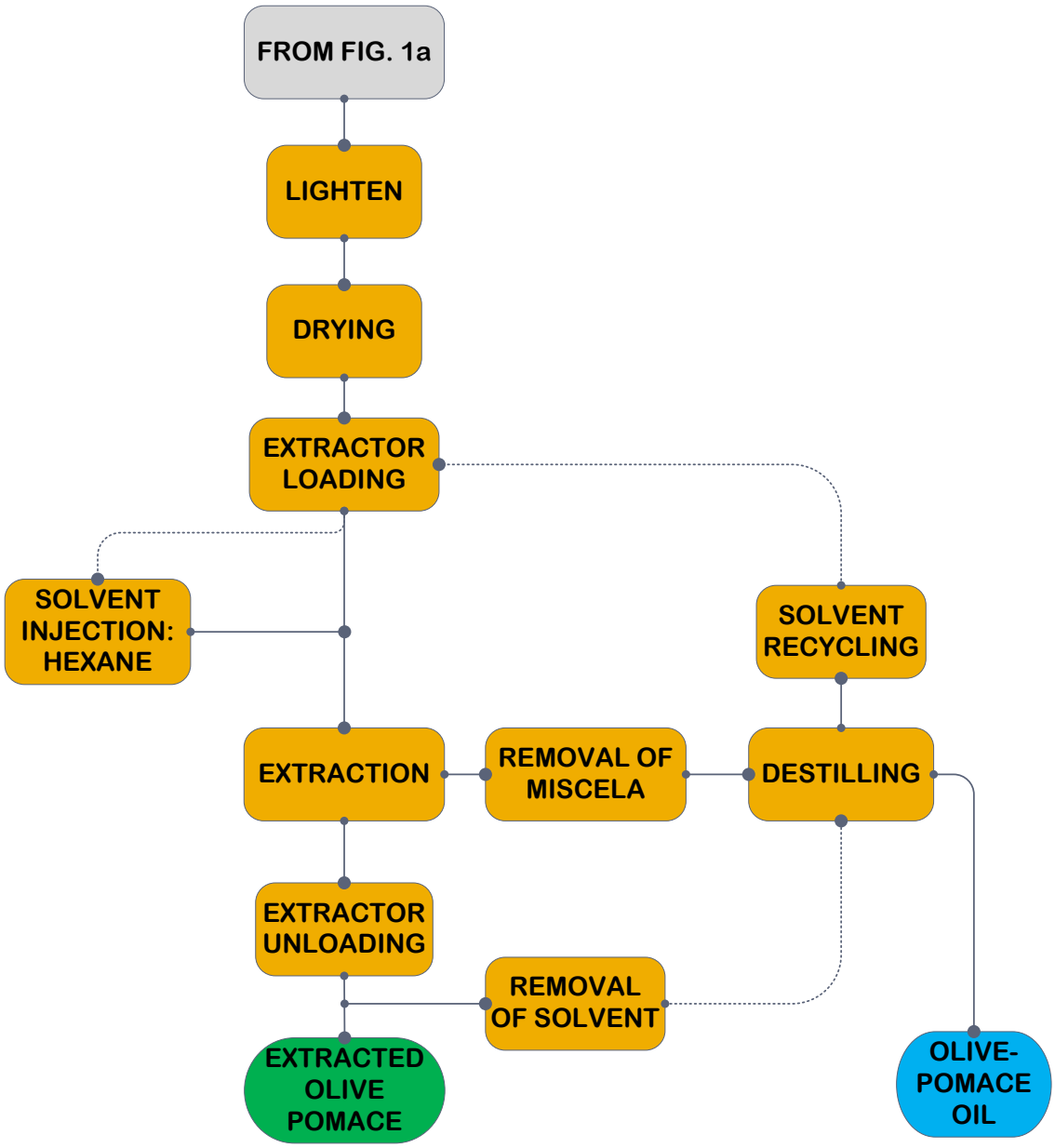


Fig. 1b. Olive oil production flowchart: olive pomace extractor (mass transfer method).

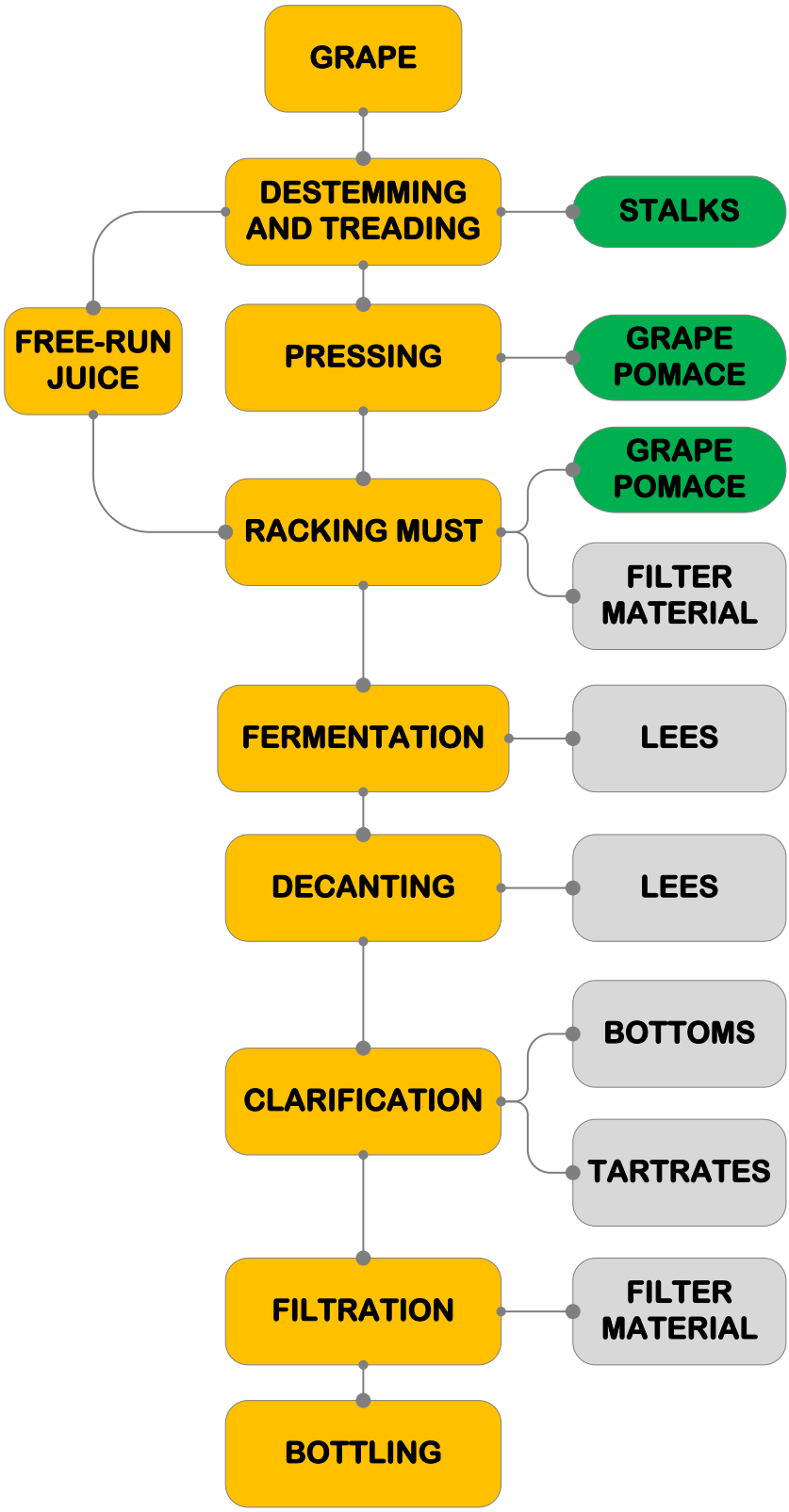


Fig. 2. White wine production flowchart.

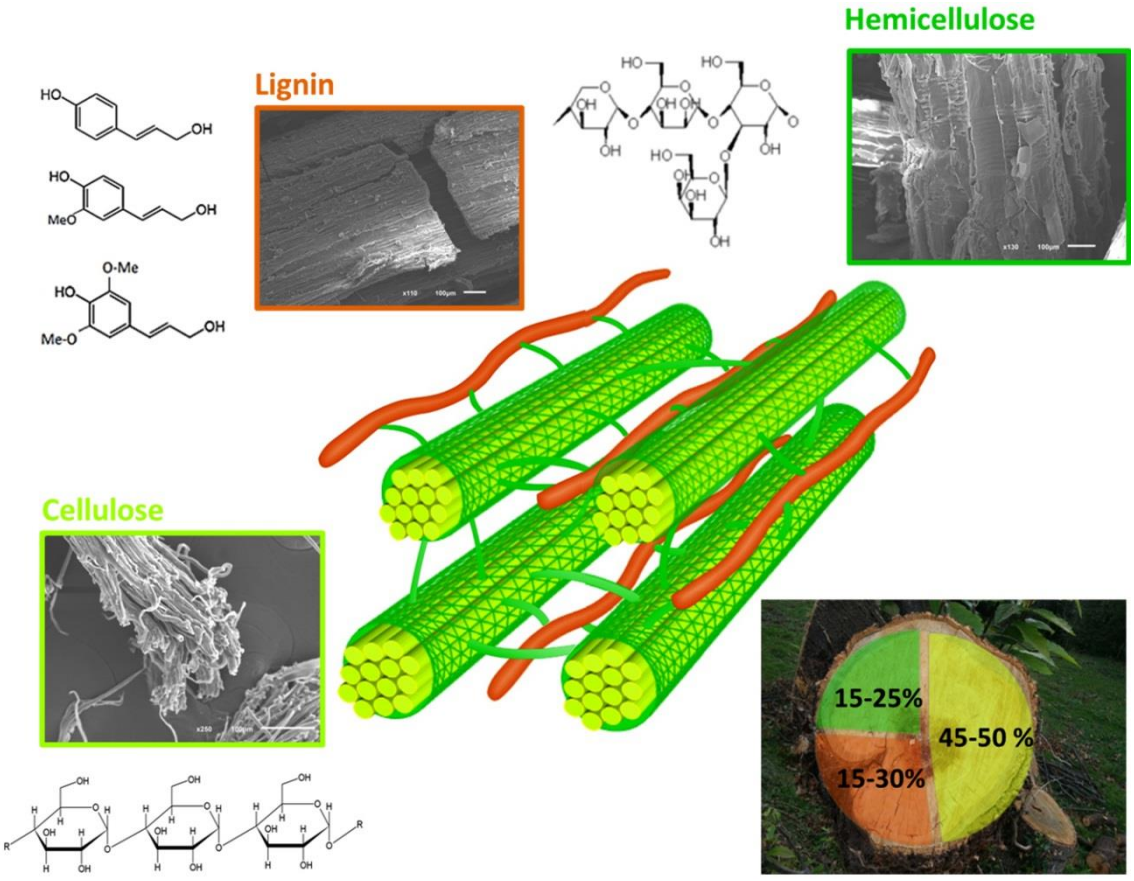


Fig. 3. 3D biomass structure

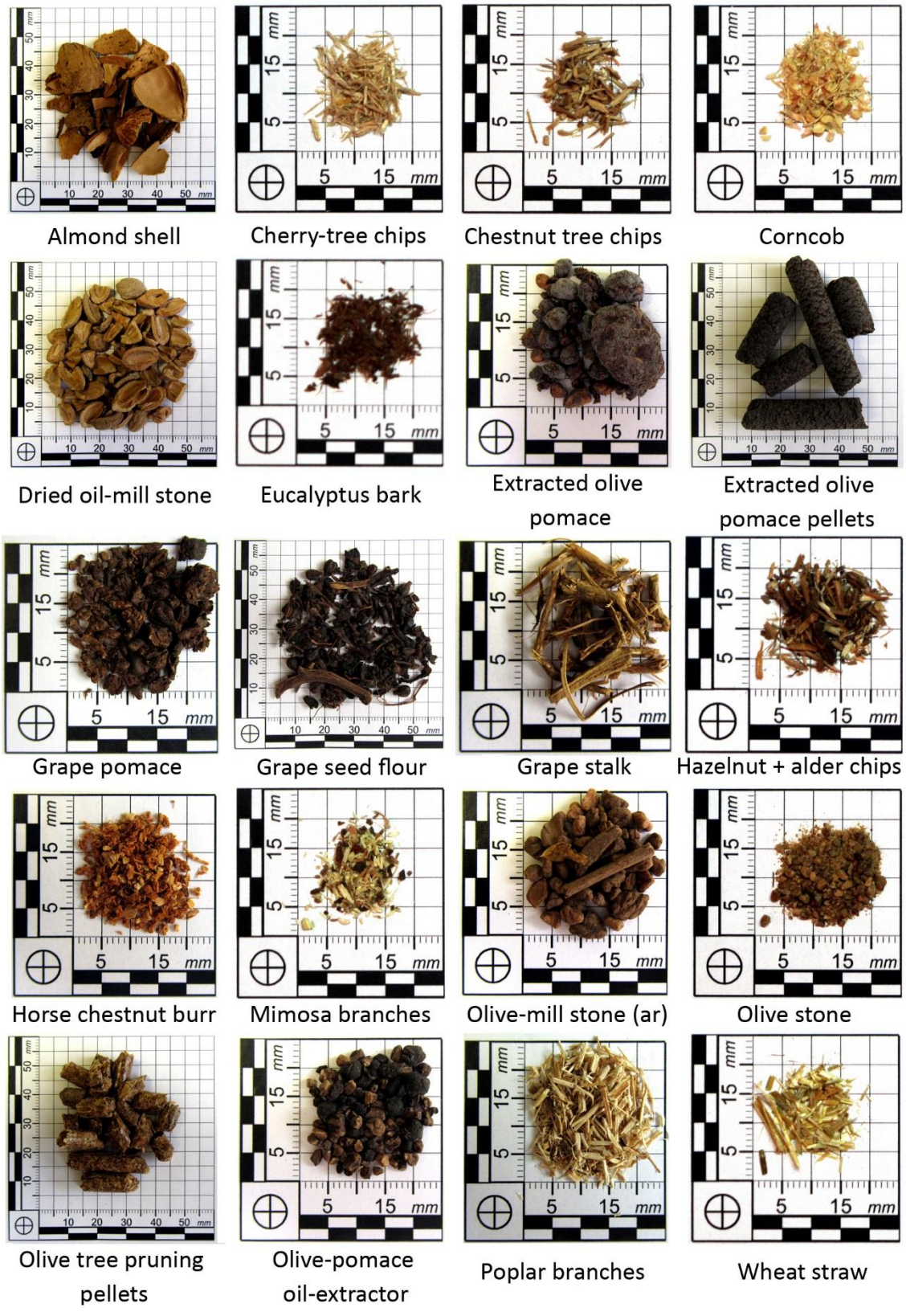
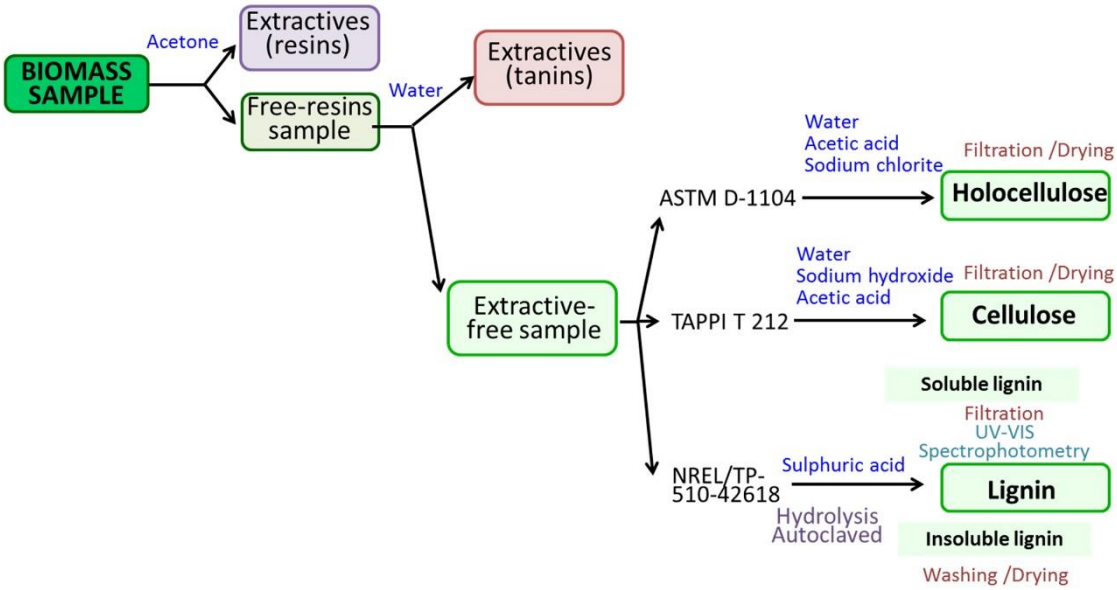


Fig. 4. Pictures of the samples analysed.



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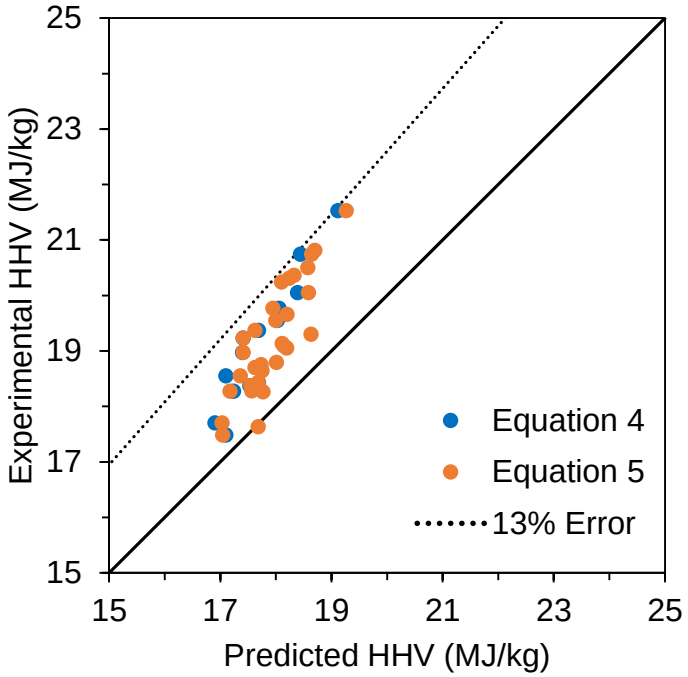
454 **Fig. 5.** Experimental procedure chart.



455

456 **Fig. 6.** Predicted vs. experimental HHV from data in the bibliography.

457 **Table 1.** Available potential biomass (t/year) and average production cost (€/t)

458 in Spain (IDAE, 2007)

Origin		**Biomass (t/year)**	**Biomass (tep/year)**	**Average costs (€/t)**
Existing forest areas	Wood harvesting remains	2 984 243	636 273	25.59
	Whole tree harvesting	15 731 116	3 414 158	43.16
Agricultural residues	Herbaceous	14 434 566	6 392 631	20.97
	Woody	16 118 220		
Herbaceous biomass susceptible to implementation in agricultural land		14 737 868	3 593 148	53.39
Woody biomass susceptible to implementation in agricultural land		6 598 861	1 468 173	36.26
Woody biomass susceptible to implementation in forest land		15 072 320	1 782 467	42.14
Total potential biomass in Spain		**88 677 193**	**17 286 851**	

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461 **Table 2.** Structural composition-based models (Callejón-Ferre et al., 2014).

AUTHOR	CORRELATION (HHV, MJ/kg dry basis)	COMMENTS
S&D (Shafizadeh et al., 1976)	HHV=0.17389[Ce]+0.26629[L]+0.32187[E]	Lignocellulosic biomass.
TIL (Tillman, 2012)	HHV=0.17389[Ce]+0.26629(100-[Ce*])	Woody biomass.
WHI (White, 1987)	HHV=17.9017+0.07444[L*]+0.0661[E*][a]	Not extracted wood. Neither R^2_{ajust}, not SE available
	HHV = 17.6132 + 0.0853[L*][a]	Extractive free wood. Neither R^2_{ajust}, not SE available
	HHV = 17.4458 + 0.0907[L*][a]	Extractive free softwood. Neither R^2_{ajust}, not SE available
	HHV = 18.0831 + 0.0637[L*][a]	Extractive free hardwood. Neither R^2_{ajust}, not SE available
	HHV = 17.7481 + 0.0800[L*](100-[E])/100 + 0.0886[E][a]	Not extracted wood. Neither R^2_{ajust}, not SE available
J&G (Jiménez and González, 1991)	HHV=(1-[Ash]/([Ce] + [L] + [E]))(0.17389[Ce] + 0.26629[L] + 0.32187[E])	Vegetal biomass. Neither R^2_{ajust}, not SE available
DEM_{01} (Demirbaş, 2001)	HHV**=0.0889[L**] + 16.8218	Vegetal biomass. SE not available
	HHV**=0.0893[L**] + 16.9742	Wood and bark. SE not available
	HHV**=0.0877[L**] + 16.4951	Not woody vegetal biomass. SE not available
DEM_{02} (Demirbas, 2002)	ΔHHV = 0.00639[E]2 + 0.223[E] + 0.691	Vegetal biomass. SE not available.
DEM_{03} (DEMİRBAŞ, 2003)	HHV**=0.0864[L**] + 16.6922	Bark and shell. SE not available
DEM_{04} (Demirbas, 2004)	ΔHHV = 0.383[E]-0.0387	Vegetal biomass. Neither R^2_{ajust}, not SE available
ACA (Acar and Ayanoglu, 2012)	HHV = 0.0979[L] + 16.292	Vegetal biomass. SE not available

Ce: cellulose + hemicellulose; L: lignin; E: extractive both measured in dry basis percentage
* Indicates composition (%) in dry and extractive free basis.
** Indicates composition (%) in dry ash free and extractive free basis.
Not SE: not standard error available.
[a] These correlations can be converted to MJ/kg as: 1 Btu/lb = $2{,}3261 \times 10^{-3}$ MJ/kg.

462 Table 3. HHV data used in this article (García et al., 2014a) and (García et al.,

463 2014b).

Sample	HHV (kJ/kg)
Almond shell	18.275
Cherry-tree chips	17.595
Chestnut tree chips	17.485
Corncob	17.344
Dried oil mill stone	18.092
Eucalyptus bark	17.752
Extracted olive pomace	18.186
Extracted olive pomace pellets	18.182
Grape pomace	17.019
Grape seed flour	16.467
Grape stalk	18.809
Hazelnut +alder chips	17.555
Horse chestnut burr	17.165
Mimosa branches	16.237
Oil-mill stone (ar)	16.484
Olive stone	17.884
Olive tree pruning pellets	18.720
Olive-pomace oil-extractor	18.687
Poplar branches	18.411
Wheat straw	17.692

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465 **Table 4.** Chemical composition of biomass samples obtained by chemical

466 extraction.

Sample	E[a]	HoloC[b]	C[b]	HemiC[b]	I.L.[b]	S.L.[b]
Almond shell	8.02	69.12	55.07	14.05	28.37	2.51
Cherry-tree chips	1.88	75.64	46.51	29.13	22.13	2.23
Chestnut tree chips	0.35	72.61	43.39	29.22	24.74	2.65
Corncob	8.72	72.50	29.71	42.79	24.49	3.02
Dried oil mill stone	2.30	72.61	50.31	22.30	25.79	1.61
Eucalyptus bark	11.30	65.73	37.31	28.42	32.37	1.90
Extracted olive pomace	67.79	57.27	27.60	29.67	38.89	3.84
Extracted olive pomace pellets	55.96	62.58	31.05	31.53	34.25	3.17
Grape pomace	26.06	46.76	28.83	17.93	51.74	1.50
Grape seed flour	9.82	53.55	37.75	15.80	45.54	0.91
Grape stalk	39.34	46.37	43.97	2.40	51.80	1.83
Hazelnut +alder chips	12.30	65.84	34.77	31.08	31.92	2.23
Horse chestnut burr	43.66	62.85	44.82	18.03	36.05	1.11
Mimosa branches	16.81	68.68	40.18	28.51	29.76	1.56
Oil-mill stone (ar)	7.99	71.96	44.72	27.24	26.51	1.53
Olive stone	2.98	69.61	58.93	10.68	28.64	1.75
Olive tree pruning pellets	13.51	71.47	59.05	12.42	27.55	0.98
Olive-pomace oil-extractor	36.84	68.24	38.20	30.04	29.31	2.45
Poplar branches	8.02	72.97	46.16	26.81	25.63	1.40
Wheat straw	25.70	75.73	38.56	37.17	21.71	2.56

467 **Table 5.** P and R coefficients matrix (chemical extraction and TG).

R matrix			
HHV	Lignin	Hemicellulose	Cellulose
1.0000	0.8291	-0.6686	0.0740
P matrix			
HHV	Lignin	Hemicellulose	Cellulose
1.0000	0.0009	0.0175	0.8191

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469 **Table 6.** Equations based on chemical composition.

	Equation	AAE (%)	ABE (%)	AAD
4	HHV=17.0704+0.0449·L-0.0202·H	0.87	0.02	0.15
5	HHV=16.1964+0.0555·L	1.13	0.02	0.20

L: lignin; H: hemicellulose (measured in mass percentage in dry ash and extractives free basis); HHV: higher heating value (MJ/kg in dry basis).

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